2020 DOE VTO Annual Merit Review

Novel Chemistry: Lithium Selenium and Selenium Sulfur Couples

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Presenter: Gui-Liang Xu

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Project ID: bat280

Overview

Timeline

- Start - October 1st, 2015.
- Finish - September 30, 2021.
- 85% Completed

Barriers

- Barriers addressed
  - Shuttle effect
  - Low electronic conductivity and low active material loading
  - Lithium dendrite and safety
  - Cycle life

Budget

- Total project funding
  - DOE share: $2500K
- Funding received in FY16-FY19:
- 2000K
- Funding for FY20: $500K

Partners

- Project lead: Khalil Amine
- Interactions/collaborations:

- **Dr. C. J. Sun (APS, ANL)** XAFS Characterization
- **Dr. Y. Ren (APS, ANL)** HEXRD characterization
- **Dr. A. Ngo, Dr. L. Cheng and Dr. L. Curtiss (ANL)** Computational modeling
- **Prof. Andy Sun (Western University)** Surface coating

Relevance and project objectives

- **Objective:** develop novel S_xSe_y cathode materials for rechargeable lithium batteries with high energy density and long life as well as low cost and high safety.
- **Impact**

This technology, if successful, will lead to:

- A cell with nominal voltage of 2 V and energy density of 600 Wh/kg
- A battery capable of operating for 500 cycles with low capacity fade

Milestones

Time	Description (status)
Oct 2019	Investigated the Li stripping/plating behaviors of Li metal in DME and HFE based electrolytes using Li/Cu and symmetric Li/Li cells (*Completed*)
Jan 2020	Investigate the impact of carbon pore structure on the active material loading and performance (*Completed*)
Jan 2020	Optimizing the content of Se doping in SeS_x/carbon composites (*Completed*)
Apr 2020	Optimizing the E/S ratio to achieve optimal trade-off between specific capacity and overall energy density (*Completed*)
Apr 2020	Demonstration of high areal capacity SeS_x/Carbon cathode (> 3 mAh cm^{-2}) with stable cycle life (*Completed*)

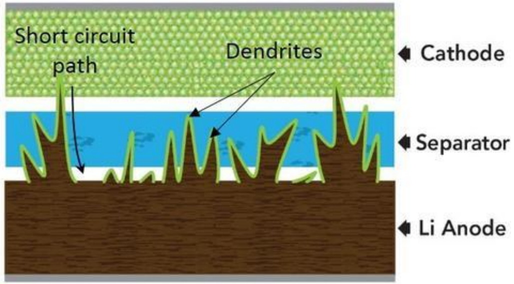
Approach

- Doping Se on S to improve electronic conductivity and increase active material loading
- Investigate the impact of carbon pore structure on the active material loading and performance
- Develop novel electrolytes to suppress dissolution of polysulfide & selenide species and prevent lithium dendrite formation
- Use in-operando synchrotron X-ray and spectroscopy probes to understand failure mechanism
- Deploy advanced modeling capability to complement diagnostic results

Technical accomplishments

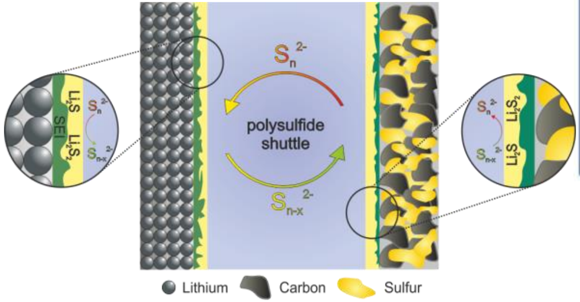
- Enable stable and fast Li stripping/plating of Li metal by using fluorinated ether-based electrolytes
- Design a new hollow carbon host for high Se-S loading to achieve high areal capacity loading (> 3 mAh cm^{-2}) with minimal shuttle effect
- Elucidate the role of Se doping on enhancing the reaction kinetics of Li-S batteries

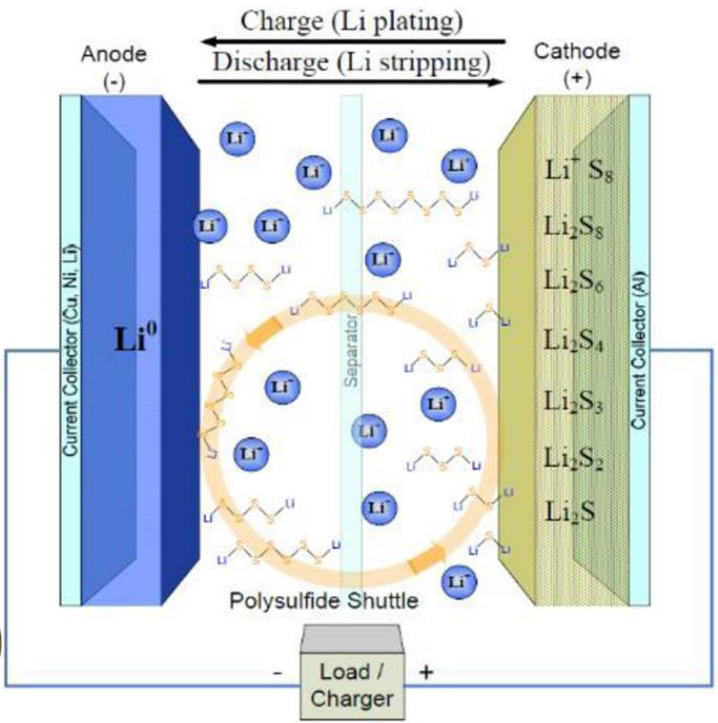
Challenges of lithium/sulfur batteries



Lithium dendrite growth

Polysulfides shuttle





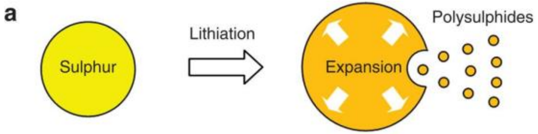
Nat. Commun. 2013, 4, 1331.
Chem. Rev. 2014, 114, 11751.
Nat. Commun. 2014, 5, 4759.
Adv. Energy Mater. 2015, 5, 1500408

Low electronic conductivity of sulfur (~10^{-30} S cm^{-1}) and Li_2S_2/Li_2S.

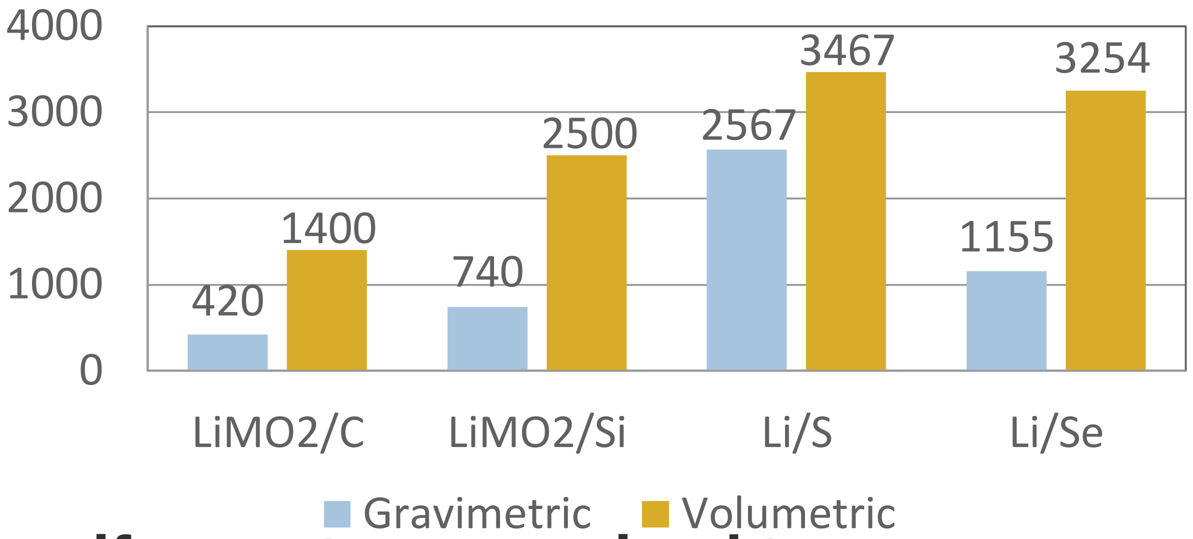
Low mass-loading of sulfur

Self-Discharge

Volume changes



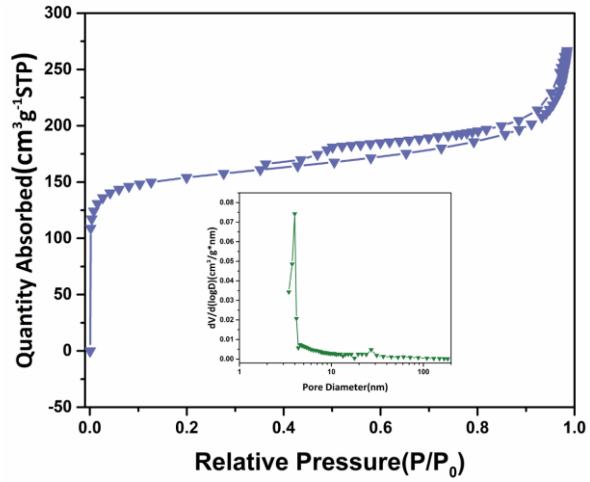
Motivation for selenium-sulfur chemistry



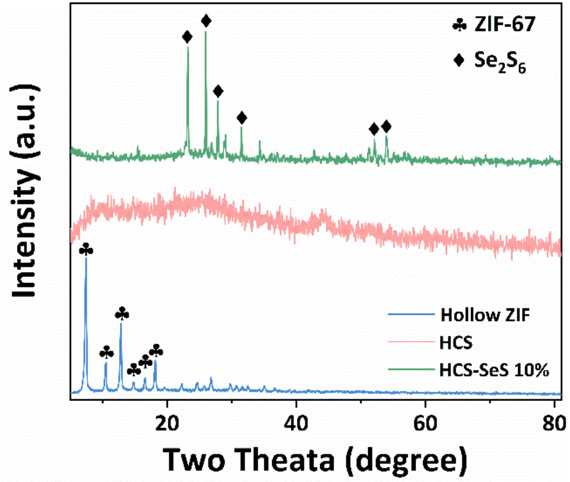
Selenium sulfur systems can lead to:

- Comparable energy density to Li/S battery
- High electrical conductivity (1E^{-3} vs. 5E^{-28} S/m for S), leading to high utilization
- High active material loading, leading to high volumetric energy density

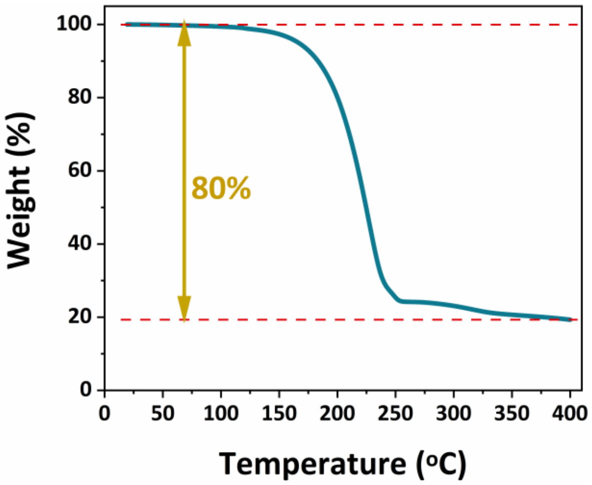
Design a new hollow carbon host to encapsulate 80 wt.% SeS_x loading in the composites



BET showed the mesoporous structure of ZIF-67 derived hollow carbon spheres (HCS)

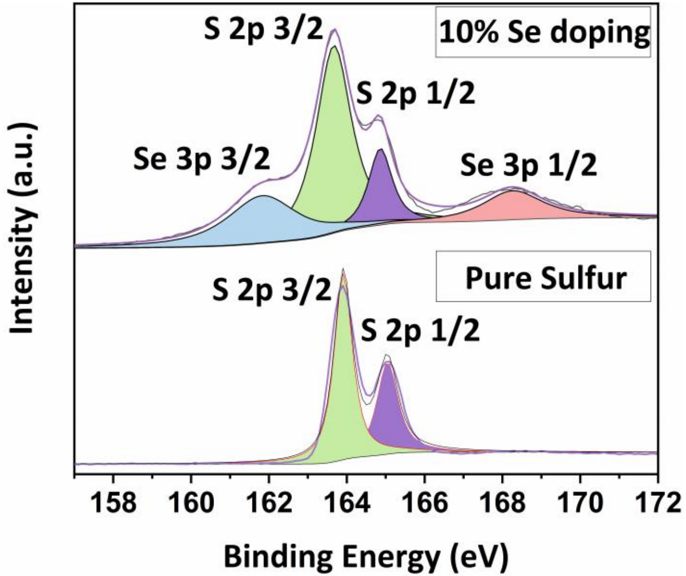


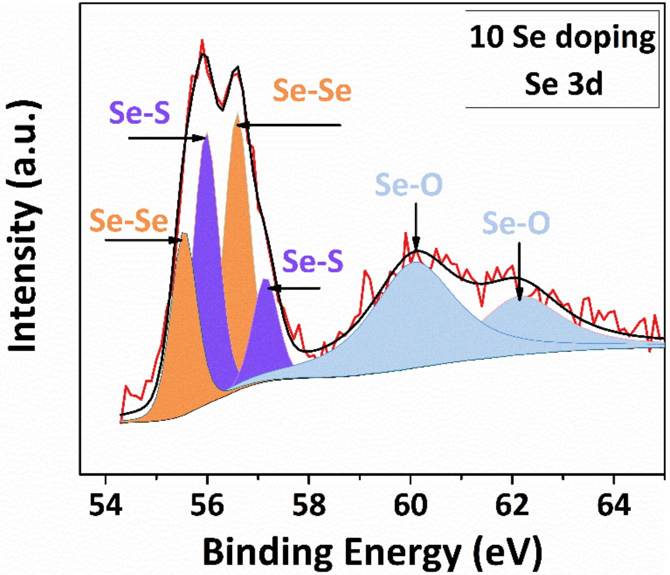
XRD showed the encapsulation of SeS_x in the ZIF-67 derived HCS



TGA confirmed 80 wt.% SeS_x loading in the composite.

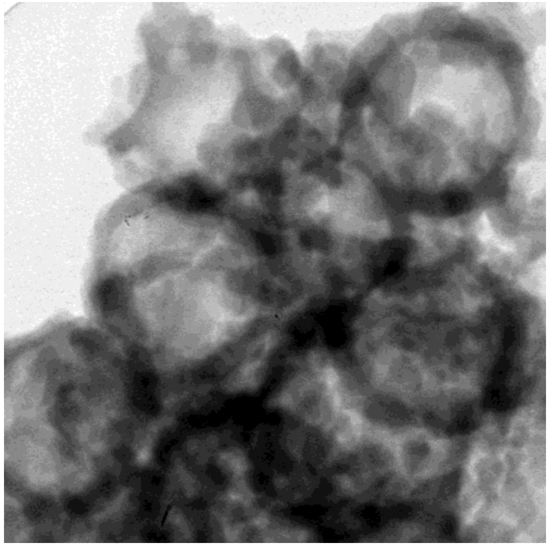
X-ray Photoelectron Spectroscopy (XPS) confirmed the formation of Se-S bond in the as-prepared SeS_x/HCS composites



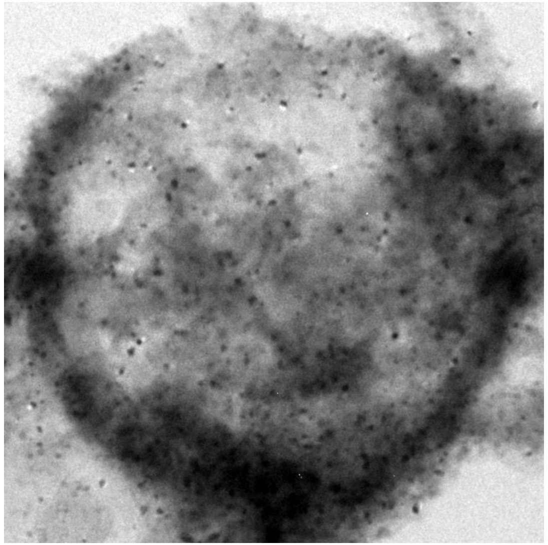


- Se-S bond indicated the formation of new SeS_x compounds rather than mixture of Se and S during melt-diffusion process.

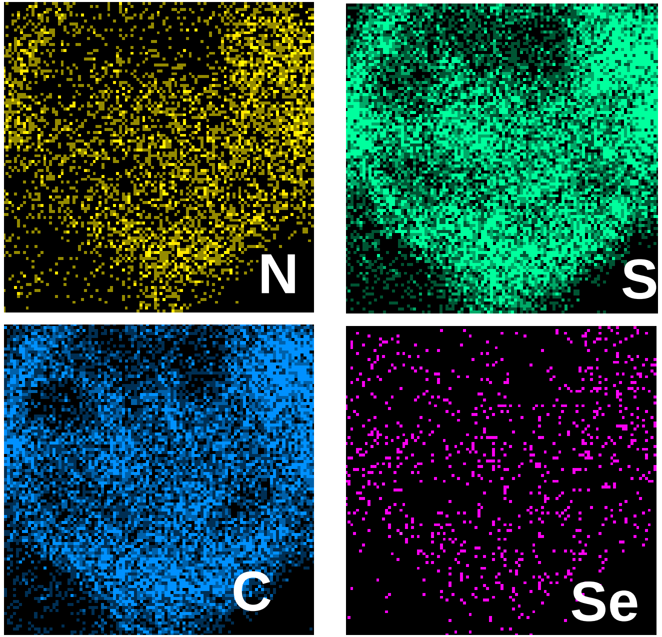
TEM and the elemental mapping showed the uniform distribution of Se and S in the composite



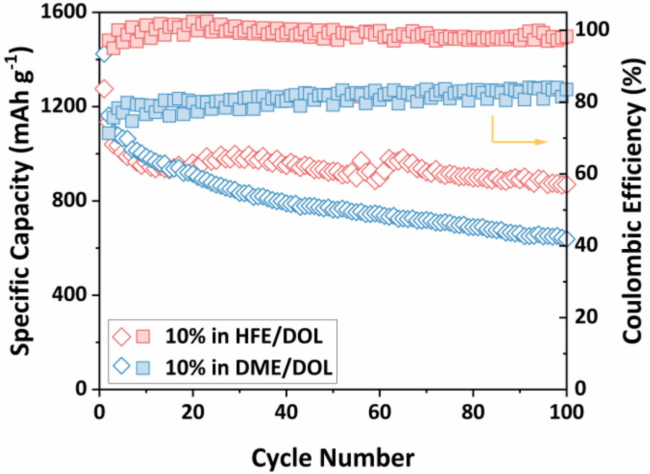
HCS

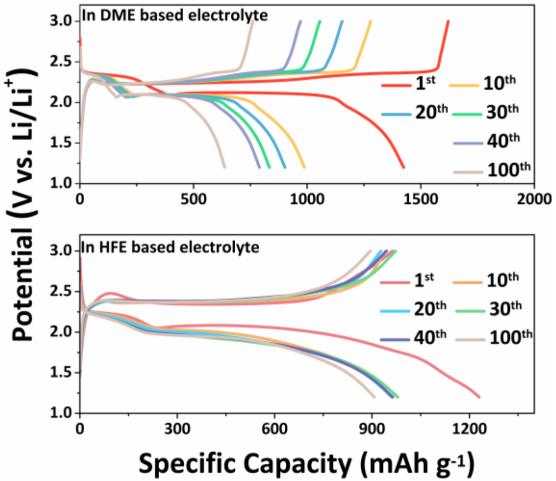


10wt.% Se doped SeS_x/HCS



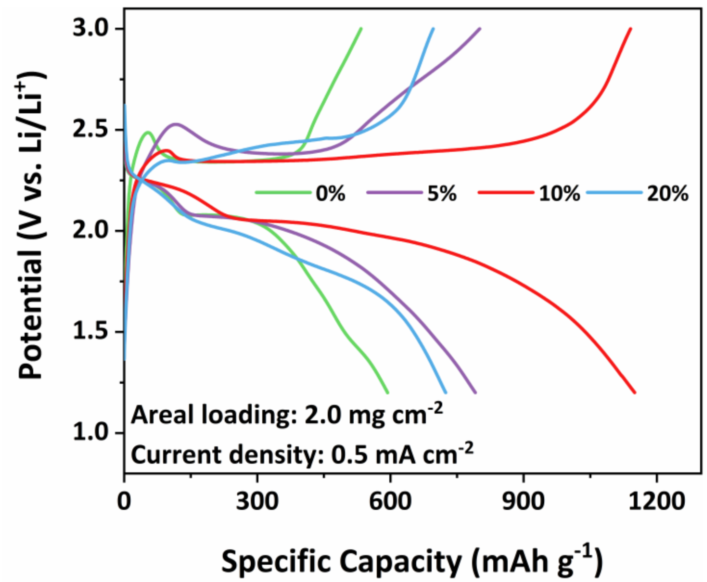
Fluorinated ether electrolytes can significantly suppress the shuttle effect and improve the cycle stability of SeS_x/HC composites

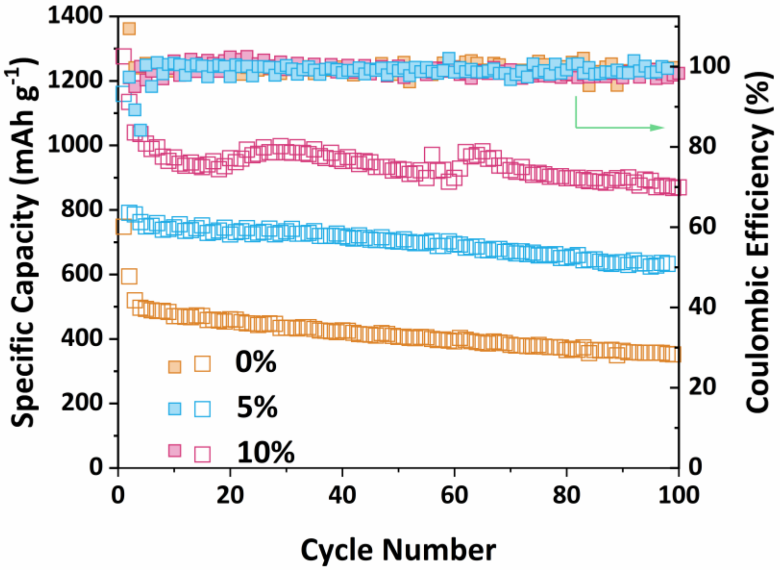




- Continuous capacity degradation and severe shuttle effect in the conventional dimethoxyethane (DME) based electrolytes;
- No visible shuttle effect and stable cycle life in hydrofluoroethers (HFE) electrolytes

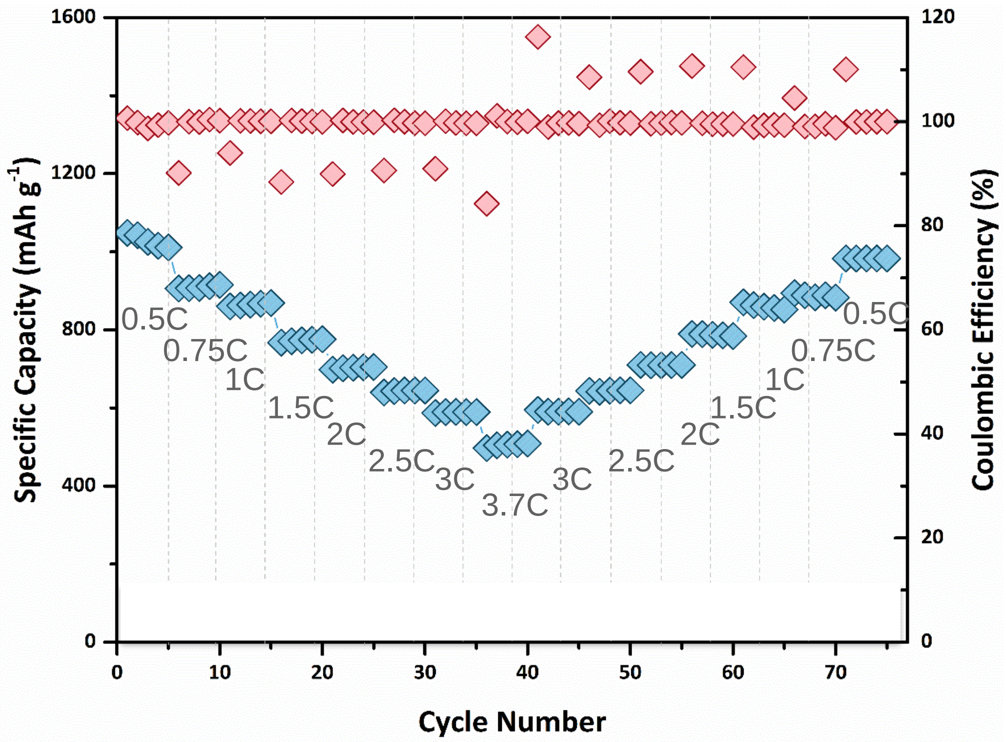
Se doping significantly improve the reversible capacity during cycling





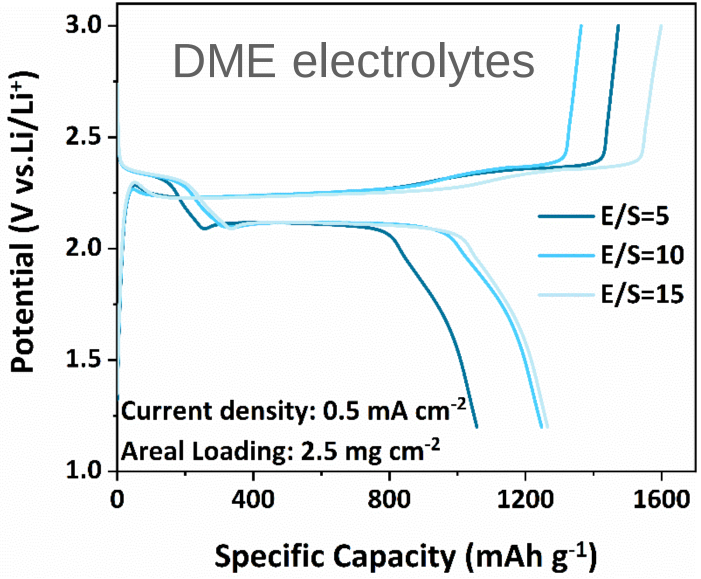
- Se doping significantly improved the utilization of active materials during cycling

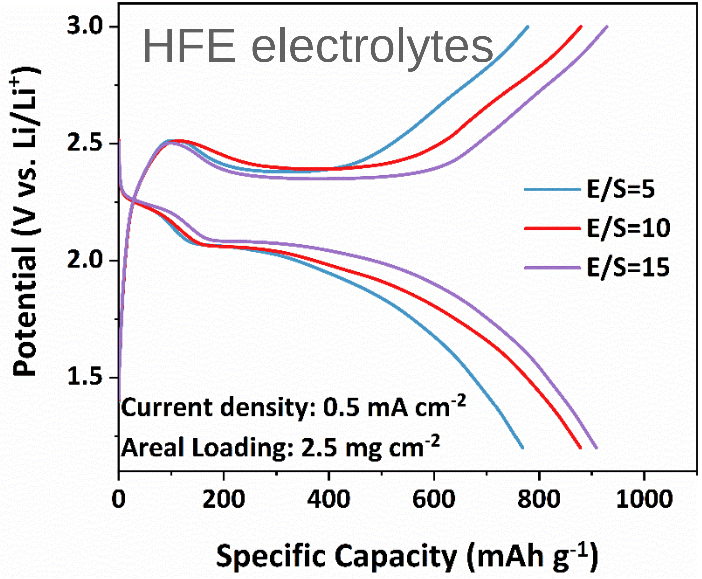
Se doping SeS_x cathode demonstrated superior rate capability in fluorinated ether electrolytes



- 10wt.% Se doped SeS_x/HCS composite demonstrated superior rate capability as Se significantly boost the reaction kinetics

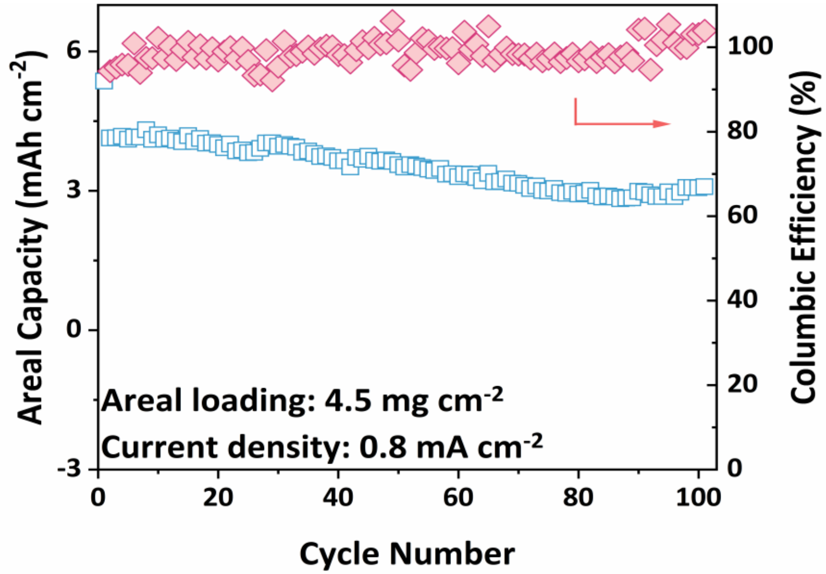
Optimization on the E/S ratio to achieve an optimal trade-off between specific capacity and overall energy density

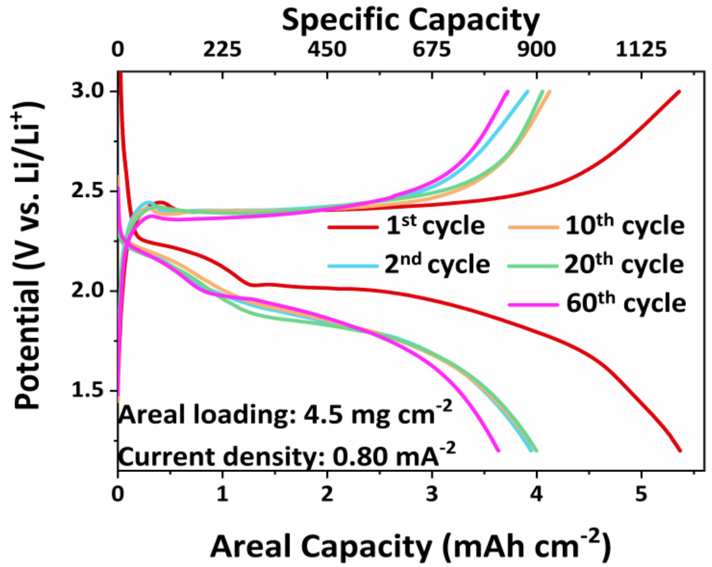




- DME: Low E/S ratio caused low capacity and severe shuttle effect
- HFE: no visible shuttle effect

Demonstration of high areal capacity loading (> 3 mAh cm^{-2}) in SeS_x/HCS cathode in fluorinated ether electrolytes

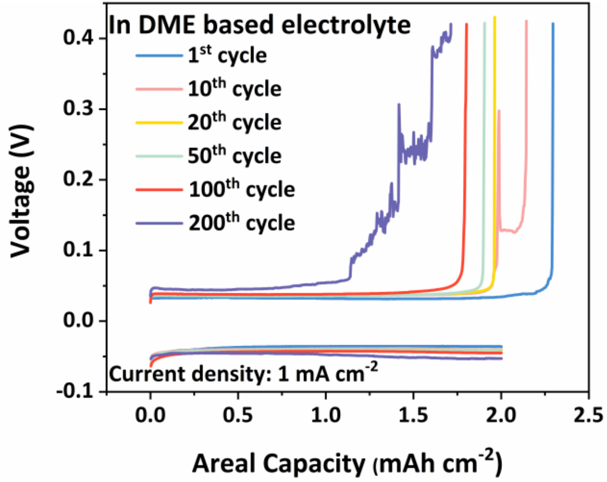




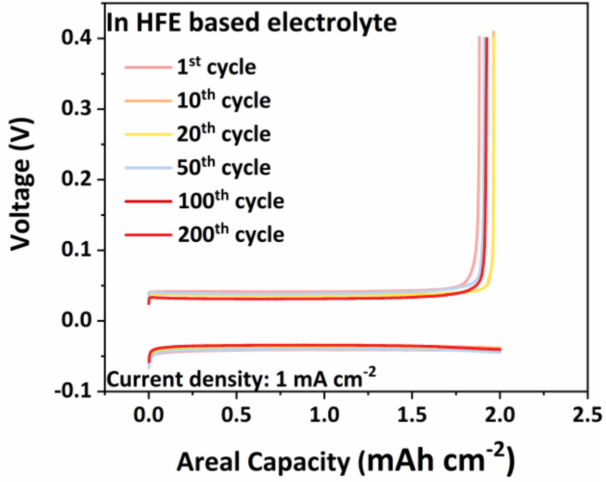
- Synergistic effect of Se doping and fluorinated ether electrolytes can enable high areal capacity loading and stable cycle life.

Demonstration of stable Li plating/stripping in fluorinated ether electrolytes

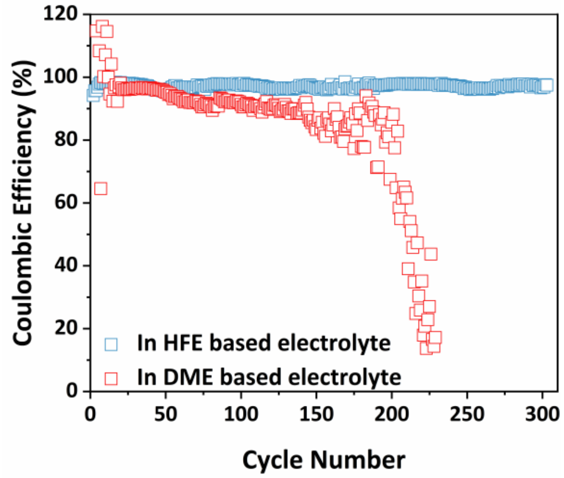
Charge-discharge curves of Li-Cu cell in DME-based electrolyte



Charge-discharge curves of Li-Cu cell in HFE-based electrolyte

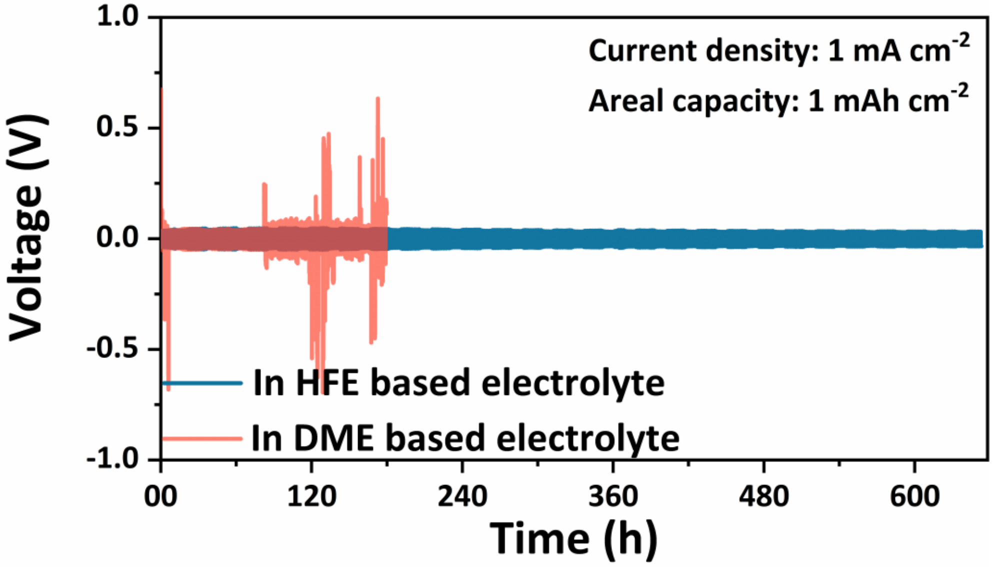


Cycling performance of Li-Cu cells in HFE- and DME-based electrolyte



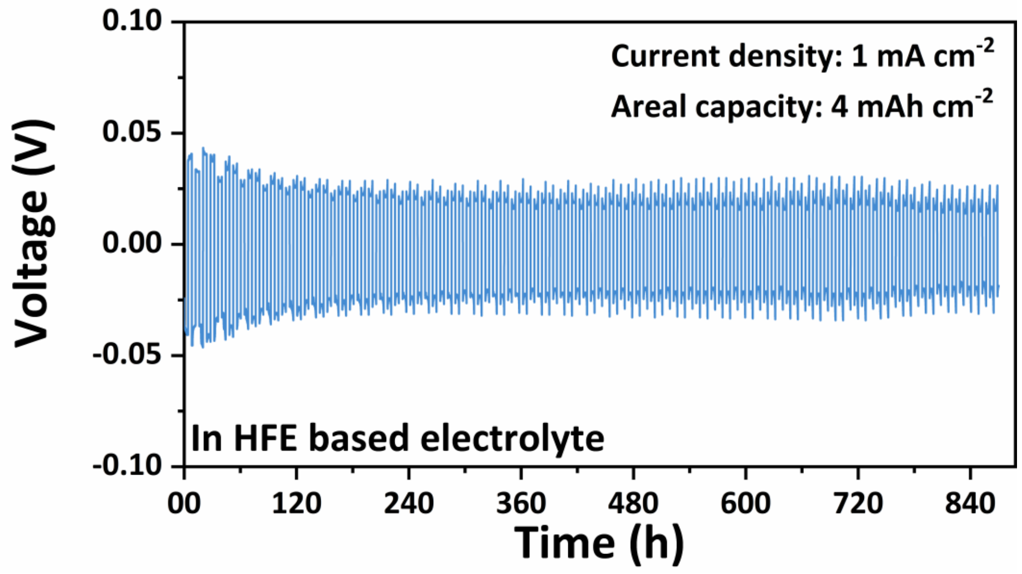
- Fluorinated ether electrolytes exhibited better Li plating/stripping stability than conventional DME electrolytes.

Better Li plating/stripping stability of fluorinated ether electrolytes than conventional DME based electrolytes in Li/Li symmetric cells



- Fluorinated ether electrolytes exhibited better Li plating/stripping stability than conventional DME electrolytes.

Stable Li plating/stripping in Li/Li symmetric cells under high areal capacity loading (4 mAh cm^{-2}) in fluorinated ether electrolytes



- Fluorinated ether electrolytes exhibited stable Li plating/stripping even under high areal capacity loading (4 mAh cm^{-2}).

Responses to Previous Year Reviewers' Comments

- No comments from the reviewers

Collaborations

- Dr. C. J. Sun (APS, ANL)
  - Mechanistic study on the capacity fade of Se and S_xSe_y cathodes using operando XAFS.
- Dr. Y. Ren (APS, ANL)
  - Mechanistic study on the capacity fade of Se and S_xSe_y cathodes using operando HEXRD.
- Dr. A. Ngo, Dr. L. Cheng and Dr. L. Curtiss (MSD, ANL)
  - Ab initio molecular dynamics simulation and DFT calculation.
- Prof. Andy Sun (Western University)
  - ALD and MLD surface coating

Remaining Challenges and Barriers

- The fast charging performance remains challenging due to the sluggish reaction kinetics in Li/Se-S batteries
- The cathode-electrolyte interfacial chemistry need to be further understood and tailored by cathode design and the use of advanced electrolytes
- Electrochemical performance of Li/Se-S batteries using thin Li metal and lean electrolytes need to be further improved to achieve high overall energy density

Proposed Future Work for FY 2020 and FY2021

- FY 2020 Q3 Milestone:
  - Interfacial understanding on cycled cathodes using TOF-SIMS
- FY 2020 Q4 Milestone:
  - Interfacial understanding on cycled Li metal using TOF-SIMS
- FY2021 work proposed
  - Develop high electrode areal loading Se-S systems (5-6 mAh cm^{-2}) developing new electrolytes and cathode structures
  - Computational understanding on the reactions kinetics and binding strength of cathode/electrolytes interaction
  - Demonstration of Li/Se-S pouch cells under lean electrolytes operation

Any proposed future work is subject to change based on funding levels

Summary

- Fluorinated ether-based electrolytes can enable much better Li plating/stripping stability than conventional DME electrolytes
- Fluorinated ether-based electrolytes can significantly suppress the shuttle effect
- Se doping significantly improve the reaction kinetics and utilization of S cathode materials during charge/discharge
- Synergistic effect of Se doping and fluorinated ether electrolytes could enable high areal capacity loading (> 3 mAh cm^{-2}) with stable cycle performance for Li/Se-S batteries.